

## Short Communication

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# Immobilization method for polyethylene glycol using a cross-linking co-agent

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### ABSTRACT

A cross-linking co-agent was used in the immobilization of polyethylene glycol (PEG) 20M peroxide to produce a capillary column for gas chromatography. The co-agent promoted the immobilization of PEG 20M and the concentrations of peroxide necessary to achieve over 80% non-extractability decreased from 15% for PEG 20M immobilization by the peroxide alone to 5 and 3% for PEG 20M immobilization using 3 and 5% of the co-agent in PEG 20M, respectively. The use of the co-agent suppressed the decrease in column efficiency and the increase in column polarity which occur in immobilization using the peroxide alone. The co-agent also increased the thermostability of the column. The mechanism of the participation of the co-agent in the immobilization of PEG 20M is discussed.

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### INTRODUCTION

The immobilization of the stationary phase is an important process in the preparation of capillary columns for gas chromatography as it makes the stationary phase film both stable and durable [1].

Methyl silicone stationary phases such as SE-30 can easily be immobilized by cross-linking the methyl side-chains of the stationary phase with peroxides such as dicumyl peroxide (DCUP). However, polyethylene glycol (PEG), which is an important stationary phase owing to its unique separation characteristics, is not easy to immobilize with peroxide alone [2–8].

Bystricky [8] reported that with 20% (w/w) of the DCUP of PEG 20M, only 65% of Carbowax 20M could be immobilized on a glass capillary column under optimum conditions. Double the amount of peroxide and a 20°C higher temperature are necessary to achieve immobilization greater than 90°C. Several alternative immobilization methods specific to PEG have been developed [4,7].

In the peroxide cross-linking of rubber or plastics, a cross-linking co-agent is

used to enhance the extent of cross-linking and consequently to improve the physicochemical properties, such as thermostability, of the rubber or plastics.

In this study, the use of a cross-linking co-agent in the immobilization of PEG 20M on a glass capillary column was investigated. Triallyl isocyanurate (TAIC) was used as the cross-linking co-agent because it is typically used in the peroxide cross-linking of rubber and plastics [10].

## EXPERIMENTAL

PEG 20M was purchased from Gaskuro Kogyo. DCUP was kindly supplied by Nippon Oil and Fats. TAIC of extra pure grade was purchased from Tokyo Kasei Kogyo and used without further purification. All other chemicals were of guaranteed reagent grade and were used without further purification.

Capillaries of 1.2 mm I.D. were drawn from Pyrex glass tubes with a Shimadzu GDM-18 glass drawing machine, which was partially modified. This inner diameter was chosen as it allows the column to be easily attached to a conventional gas chromatograph for packed columns without any alterations.

After the capillary had been treated with 6 *M* hydrochloric acid for 1 h and rinsed successively with water and methanol, it was statically coated with a solution of PEG 20M in methylene chloride containing DCUP and TAIC in various amounts. The column was flused with nitrogen gas for 1 h, sealed at both ends and was then cured at 160°C for 1 h. After cutting both ends of the column to give a length of 40 m, the fused-silica capillaries (30 cm × 250 μm) were attached to both ends of the column through stainless-steel connectors and the column was mounted on a gas chromatograph through the ends of other fused-silica capillaries. The column was then conditioned at 180°C for 1 h and its performance was tested with standard chemicals. The column was rinsed with methylene chloride and then the column performance was tested again to determine the non-extractability of PEG 20M. The column temperature was then raised to 250°C at a rate of 5°C/min and was held at 250°C for 84 h; the performance was tested to determine the thermostability of the column.

The non-extractability and thermostability of the PEG-20M film were estimated from the changes in capacity factor of the naphthalene peak after rinsing with methylene chloride and heating the column at 250°C for 84 h, respectively.

The Kováts retention indices for benzene, butan-1-ol, pentan-2-one, nitropropane and pyridine were measured at 80°C and were summed to estimate the polarity of the column.

## RESULTS AND DISCUSSION

Fig. 1 shows the variation in extraction with DCUP concentration for the column immobilized with DCUP alone and with TAIC concentration for the columns immobilized with both DCUP and TAIC. The non-extractability increased with increasing concentration of DCUP, and a DCUP concentration greater than 15% of the weight of PEG 20M was required to achieve more than 80% immobilization with DCUP alone.

The addition of TAIC greatly enhanced the immobilization of PEG 20M on the

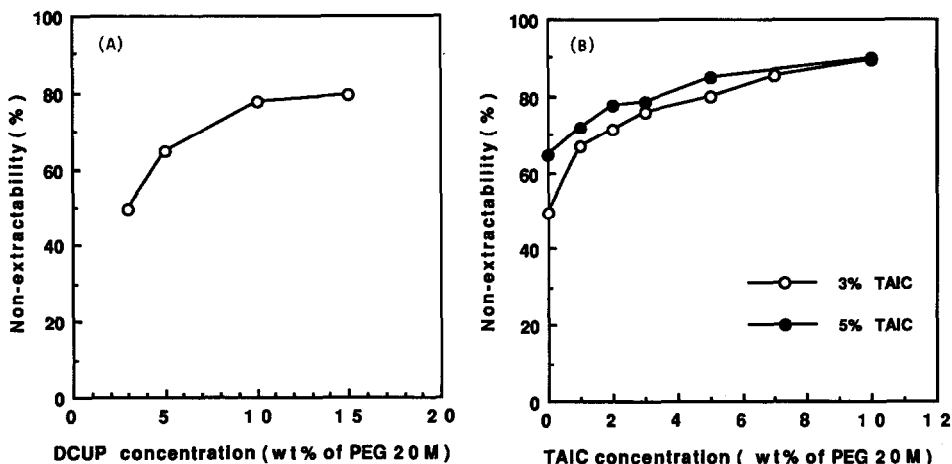


Fig. 1. Variation of non-extractability (A) with DCUP concentration for the column immobilized with (A) DCUP alone and (B) with TAIC concentration for the columns immobilized using both TAIC and DCUP. Concentrations are expressed as percentage of weight of PEG 20M.

glass capillary. For example, the addition of only 1% (w/w) TAIC increased the non-extractability from 49.4 to 67.1% with 3% (w/w) DCUP. The non-extractability increased with increasing concentration of TAIC, but the addition of an excess of TAIC (10% of the weight of PEG 20M) resulted in the tailing of all peaks tested. On the addition of 3 and 5% TAIC, the DCUP concentration required to achieve more than 80% immobilization was lowered from 15 to 5 and 3% of the weight of PEG 20M, respectively.

To examine the effect of the cross-linking co-agent on column performance, coating efficiency and thermostability, the Kováts retention indices were measured for columns with similar extractabilities prepared under three different conditions and a column which had not been immobilized.

Fig. 2 shows the Van Deemter curves for the naphthalene peak of these columns and Table I compares the performances of these columns. The optimum flow-

TABLE I

COMPARISON OF THE PERFORMANCES OF SIMILAR COLUMNS PREPARED UNDER VARIOUS CONDITIONS

Column No.	Curing conditions (%)		Non-extractability (%)	Coating efficiency (%)	$\Delta\Sigma RI^a$	$\Delta k^b$ (%)
	DCUP	TAIC				
1	—	—	—	82.8	—	—
2	15	—	79.6	67.5	65	10.2
3	3	5	80.0	74.9	27	6.5
4	5	5	84.8	71.5	37	5.4

<sup>a</sup>  $\Delta\Sigma RI$  = Deviation of the sum of the Kováts retention indices for five reference compounds from that of a non-immobilized column.

<sup>b</sup>  $\Delta k$  = Percentage decrease of the capacity factor for naphthalene after heating at 250°C for 84 h.

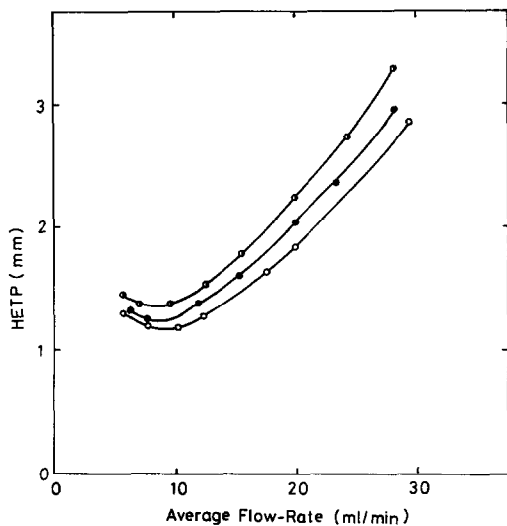


Fig. 2. Van Deemter curves of the naphthalene peak at 140°C for columns prepared under various conditions. Film thickness = 1  $\mu$ m; length = 40 m. (○) Non-immobilized column; (●) column immobilized with 15% DCUP; (●) column immobilized with 3% DCUP and 5% TAIC.

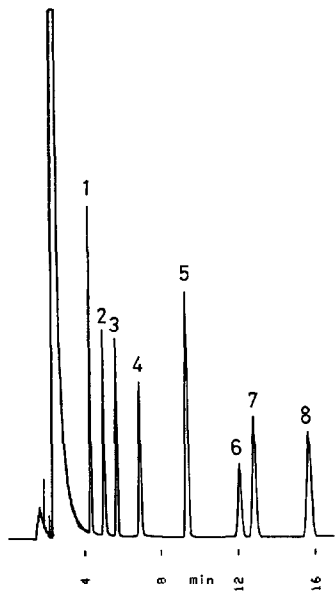


Fig. 3. Gas chromatogram of a test mixture on the column immobilized with 3% DCUP and 5% TAIC (expressed as percentage of weight of PEG 20M). Film thickness = 1  $\mu$ m; length = 40 m; column temperature = 140°C; flow-rate = 20 ml/min. Peaks: 1 = pentadecane; 2 = octan-1-ol; 3 = methylcaprate; 4 = dicyclohexylamine; 5 = naphthalene; 6 = caproic acid; 7 = 2,6-dimethylaniline; 8 = 2,6-dimethylphenol.

rate was about 8 ml/min for the 1.2 mm I.D. column. The column efficiency at the optimum flow-rate decreased with the immobilization of the stationary phase, but the magnitude of the decrease was smaller for the columns immobilized using TAIC than for those immobilized using DCUP alone.

The column was heated at 250°C for 84 h and the change in capacity factor for the naphthalene peak was measured to evaluate the thermostability of the column. For the non-immobilized column, the stationary phase formed droplets during heating and the column efficiency decreased significantly. For the immobilized columns, no changes in the appearance of the stationary phase, peak shapes of standard chemicals nor column efficiency were observed, except for the decrease of the capacity factor. The use of TAIC reduced the decrease in the capacity factor for the naphthalene peak on heating at 250°C for 84 h to about 60% of that for the column immobilized with DCUP alone. This corresponds to the extension of the column lifetime from 540 to 940 h during one half-life.

The use of TAIC also depressed the increase in column polarity, which was frequently observed in the immobilization of PEG with peroxide and caused changes in the separation pattern of complex mixtures such as polyunsaturated fatty acids [4,5,9]. Table I shows the deviations of the sum of Kováts retention indices for five reference compounds for columns with very similar non-extractabilities from that of a non-immobilized column. The deviations for the columns immobilized using both TAIC and DCUP were less than 50% of the value for the column immobilized with DCUP alone.

Fig. 3 shows a chromatogram of the test mixture containing various types of compounds. All the peaks were symmetrical and no tailing was observed for the peaks of acidic or basic compounds, which indicates that the column was deactivated satisfactorily.

In conclusion, the use of a cross-linking co-agent in the immobilization of PEG 20M increases the efficiency and thermostability of the column and decreases the change in column polarity caused by the immobilization. The column is deactivated satisfactorily and can be used for the determination of various types of compounds.

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